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VOL. XLI] SECTION A [No. 5

MAY 1955

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INFLUENCE OF THE DEGREE OF PERFECTION OF A CRYSTAL ON THE INTENSITY OF BRAGG REFLECTION

Part I. Measurements with Calcite and Rocksalt

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Received March 19, 1955

(Communicated by Prof. G. N. Ramachandran, F.A.SC.)

1. Introduction

It is well known that the state of perfection of a crystal has a profound influence on the intensity of a Bragg reflection. In a mosaic crystal, the small crystalline blocks are not in exact parallel alignment with one another and therefore they will not all reflect at the same setting. Consequently the breadth of reflection and the integrated intensity will be much greater for a mosaic crystal than for a perfect one. Both these results have been used to measure the perfection or mosaicity of crystals and a good summary of such studies has been given by James (1948).

More recently Evans, Hirsch and Keller (1948) and Wooster and Macdonald (1948) have worked on these lines using the photographic film and ionisation chamber for intensity measurements. Although it has been known that the integrated intensity increases with the breadth of reflection, an exact correlation between the two has not been obtained. It must be mentioned that both these measurements are not very accurate. The breadth of reflection is a difficult quantity to measure, while measurements of absolute reflecting powers become inaccurate because of the large ratio between the intensities of the incident and reflected beams, usually of the order of 1000: 1.

A new method was suggested very recently by Ramaseshan and Ramachandran (1954) for the study of perfection of crystals, using polarised X-rays. It is based on the well-known result that the integrated intensities, when X-rays are polarised perpendicular and parallel to the plane of reflection, are in the ratio of $|\cos 2\theta|$: 1 for a perfect crystal and $\cos^2 2\theta$: 1 for an ideally mosaic crystal. This method is sensitive since it involves only a measurement of the relative intensities for two azimuths of polarisation which can be done accurately as the two are of the same order of magnitude. The

above authors also showed that the method was workable, by studying natural and ground surfaces of $NaNO_3$.

The present author has taken up a systematic study of the texture of crystals, in particular by means of polarised X-rays. Some results obtained from a study on specimens of calcite and rocksalt are reported here. It is proposed to publish fuller investigations in subsequent parts about the correlation of this method with the other methods of studying the texture of crystals.

2. EXPERIMENTAL DETAILS

The arrangement was very similar to the one adopted by Ramaseshan and Ramachandran, with some improvements, which are mentioned under appropriate sections below.

The apparatus consisted of (*a*) Polariser-monochromator; (*b*) Spectrometer assembly; (*c*) Integrating device; (*d*) Electronic equipment for Geiger counter.

(*a*) *Polariser Monochromator.*—The X-ray beam of copper Kα radiation was reflected from the 311 planes of a single crystal of copper, the Bragg angle being 45° 6′. Since the deviation is almost exactly a right angle, the reflected beam would be completely polarised. This arrangement, housed in a box, was permanently mounted on to the window of the X-ray tube and was provided with a tangential screw for occasionally adjusting the inclination of the copper crystal to the X-ray beam.

(*b*) *Spectrometer Assembly.*—An ordinary optical spectrometer was converted for this purpose. Polarised X-rays from the copper crystal passed vertically down through a collimator, fixed along the vertical axis of the spectrometer on to the crystal under study, which was mounted on a goniometer head, at the correct inclination to the beam. The Geiger counter was carried by an arm which could slide along a graduated vertical circle, with the crystal as centre and thus the counter could be set for different reflections, at appropriate positions along this circle. When the counter had been aligned for a reflection, this arm could be rigidly coupled to the crystal holder and thereafter the crystal and the counter could be rotated together about the X-ray beam as axis, through a total range of 180°, thus facilitating measurements at different azimuths from $-90°$ to $+90°$, on either side of the forward position.

(*c*) *Integrating Device.*—An arrangement was provided for rocking the crystal at a slow uniform rate through the Bragg position, by means of a reversible synchronous motor of speed 1 r.p.m., flexibly coupled to the

goniometer screw. This motor was mounted on the spectrometer base itself. The integrated intensity at any setting was thus directly obtained by recording the total number of pulses from the Geiger counter during this period, corrected for background. The motor was run forward and backward over a range of 6° and average of several runs was taken and it was possible to obtain integrated intensity measurements with an accuracy of about 5%.

This method was found more convenient and accurate than manually setting the crystal in close intervals at various inclinations to the X-ray beam and thereafter integrating the intensity readings graphically by taking the area under the reflection curve.

(*d*) *Electronic Equipment.*—A conventional scale of 128 circuit and a counting rate meter, with their associated power supplies were used for recording the pulses of the Geiger counter. The counter was an Amperex product (type 153 *C*, mica window, argon-halogen filled) requiring about 1500 volts, which was provided from a stabilised high voltage supply. The counting rate meter was used initially to set the crystal and the counter for a reflection and the total number of counts for each run was thereafter obtained from the scaling unit.

All records were made at an average rate of about 10,000 to 15,000 counts per minute at the peak of reflection, thus ensuring a good accuracy and freedom from any appreciable dead time losses. At each setting, the intensity was brought down to this counting rate by putting a suitable number of thin nickel foils in front of the mica window of the counter; the absorption factor of each set of standard foils was determined separately.

3. Results and Discussion

On the basis of the dynamical theory of X-ray reflection, the intensity of surface reflection for polarised X-rays, taking absorption of the crystal into account, was worked out in detail by Hirsch and Ramachandran (1950) and only the results relevant for discussion are cited here.

The integrated intensity of a surface reflection ρ is given, in general, by

$$\rho = \frac{K}{\pi} \frac{e^2}{mc^2} N |F| \frac{\lambda}{\sin 2\theta} R_y(g, k) \qquad (1)$$

where K is the polarisation factor,

$= 1$ for azimuth zero and

$= |\cos 2\theta|$ for azimuth 90°

λ is wavelength of X-rays,

F and θ are structure amplitude and Bragg angle of the reflection.

Here g is a parameter of value,

$$g = \frac{1}{2K} \frac{mc^2}{e^2 \lambda N} \frac{\mu \sqrt{1+k^2}}{|F|} \tag{2}$$

where μ is the linear absorption coefficient and

k is the ratio of the imaginary to the real component of F.

In equation (1), $R_y(g, k)$ is a function which depends on the state of perfection of crystal: It takes the form

$$R_{y\mathrm{M}} = \pi(1 + k^2)/4 \, |g| \tag{3}$$

for an ideally mosaic crystal and

$$R_{y\mathrm{P}} = \pi(1 + k^2)/4 \, [\{\exp - (|g| + C)\} + |g|] \tag{4}$$

where C is a numerical constant $= \log_e 32/3\pi$, for a perfect crystal.

In a perfect crystal, if absorption is neglected, *i.e.*, if $\mu = 0$, then since $|g| = 0$, we have from equation (4),

$$R_{y\mathrm{PN}} = 8/3 \tag{5}$$

Now, the ratio of the integrated intensity for azimuth 90° to the value for azimuth zero, could be obtained by combining equations (3), (4) and (5) with (1) and (2). Denoting this ratio by α, we have

$$\left.\begin{aligned} \rho_\perp/\rho_\parallel &= \alpha = \cos^2 2\theta \text{ for a mosaic crystal} \\ &= |\cos 2\theta| \text{ for a perfect crystal} \end{aligned}\right\} \tag{6}$$

These are well-known results of the dynamical theory. However due to finite absorption, α will deviate in any actual perfect crystal, from the value of $|\cos 2\theta|$ towards the mosaic value of $\cos^2 2\theta$, with increasing absorption. The value of α for an absorbing perfect crystal can be calculated from equation (4).

(*a*) *Degree of perfection.*—The degree of perfection (Δ) was defined by Ramaseshan and Ramachandran, in terms of these concepts, as

$$\Delta = \frac{r(\phi) - r_{\mathrm{M}}(\phi)}{r_{\mathrm{PA}}(\phi) - r_{\mathrm{M}}(\phi)} \tag{7}$$

where $r(\phi)$ is the ratio of the integrated intensity at any azimuth (ϕ) to that at azimuth zero and the subscripts M, PA refer to mosaic and perfect

absorbing cases. Using the experimental data for intensities at zero and 90° azimuth positions, Δ could be evaluated from equation (7).

The results of measurements on three specimens of calcite for the 422 and 633 reflections are summarised in Table I. The measurements could not be made for the 211 reflection because the spectrometer was suited to record only reflections whose Bragg angle was between 25° and 60°.

TABLE I

Data for calcite. Theoretical values were calculated by using F values at absolute zero. Integrated intensity values are in arbitrary units.

Specimen and treatment of surface	422 $F = 18{\cdot}9$ $\theta = 30°\ 30'$				633 $F = 22{\cdot}9$ $\theta = 49°\ 39'$				ρ/ρ_P for $\phi = 0°$		ρ_{633}/ρ_{422} for $\phi = 0°$
	$\rho_{\parallel}$	$\rho_{\perp}$	α	Δ	$\rho_{\parallel}$	$\rho_{\perp}$	α	Δ	422	633	
A. Ground with carborundum	46·9	12·3	·263	20%	56·9	1·48	·026	23%	1·75	1·58	1·21
B. Natural untreated ..	46·7	13·9	·298	45%	52·7	2·42	·046	46%	1·74	1·46	1·13
A. Etched slightly with dilute HCl	26·8	9·4	·352	86%	36·0	2·48	·069	96%	1	1	1·34
Perfect (theory) ..	..	..	·374	100%	..	..	·070	100%	1	1	1·14
Ideally mosaic (theory)	..	..	·235	0%	..	..	·026	0%	2·76	3·32	1·33

It is seen from the table that the natural cleavage gave a degree of perfection of 45%. This particular specimen (B) had a number of lines on the surface and was not very perfect. Grinding a natural surface reduced the perfection to about 20%; by etching the surface with dilute HCl, the surface became about 90% perfect.

(*b*) *Ratio of intensities for zero azimuth.*—From equation (1) it follows that for a particular reflection, the ratio of the intensities for a mosaic and perfect crystal is

$$\rho_M/\rho_P = R_{yM}/R_{yP} \qquad (8)$$

and this could be worked out for each reflection from equations (3) and (4). Assuming that the etched surface was almost perfect the entries in the fourth

column have been calculated and it is seen that the ratio increases with imperfection but it is less than the theoretical value of ρ_M/ρ_P because the ground surface was not ideally mosaic but had a perfection of 20%.

(*c*) *Ratio of intensities for different orders.*—Another comparison between theory and experiment would be the ratio of the intensities of two orders of reflections, for a given state of perfection, since it could be shown from equation (1) that,

$$\rho_M \propto F^2/\sin 2\theta \text{ for the mosaic case} \quad (9)$$

and

$$\rho_P \propto |F|/\sin 2\theta\,[\{\exp -(|g|+C)\}+|g|] \text{ for the perfect case} \quad (10)$$

Therefore the two orders of reflection could be compared by putting in the appropriate values of F and θ in (9) and (10). It is seen from the last column of Table I, that the ratio of the intensities of the two reflections all lie in the range predicted by theory. It will be noted that this range is quite small varying only from 1·14 to 1·33 because the F values of the two reflections are close to each other the one about 19 and the other 23. This particular comparison is not however very accurate, since the incident beam was not standardised.

(*d*) *Measurements with rocksalt.*—Results of similar measurements on rocksalt are given in Table II.

TABLE II

Rock salt 400 *and* 600 *reflections.*
F values were taken for the crystal at 290° *abs. from Renninger's data* (1952).
Intensity values in the same units as in Table I.

Specimen	400; F=50; θ=33° 13′				600; F=30; θ=55° 12′				ρ_{400}/ρ_{600} for ϕ=0°
	$\rho_{\parallel}$	$\rho_{\perp}$	α	Δ	$\rho_{\parallel}$	$\rho_{\perp}$	α	Δ	
Rocksalt ground with carborundum	213	36·1	·169	5%	91·8	12·6	·137	11%	2·66
Mosaic (Theory) ..	..	..	·160	0%	..	..	·123	0%	2·74
Perfect (theory) ..	..	..	·330	100%	..	..	·249	100%	1·84

Measurements for a natural face of rock salt could not be made as there were considerable local variations on the surface of the samples available to the author.

It will be observed, from the comparison made in the last column, that the range of the calculated ratio for perfect and mosaic crystals is larger than in calcite since the F values of the reflections are very different for rock salt, namely 50 and 30. Since the ground crystal of rock salt became almost ideally mosaic the ratio obtained by experiment of 2·66 is in close agreement with the calculated value of 2·74.

It is possible to calculate from equation (1) the ratio of the two orders of reflection for unpolarised X-rays by putting in appropriate polarisation factors for the parallel and normal components. This gives a value for the ratio ρ_{400}/ρ_{800} of 1·78 for perfect and 2·76 for mosaic crystals for unpolarised X-rays. It is interesting to note that Renninger (1934) using unpolarised X-rays obtained values varying between 2·27 and 2·76 with specimens of different perfection.

It is proposed to refine the experimental technique further by including a monitor for the monochromatic polarised beam, incident on the crystal under study and to get much better estimates of the intensities obtained with different crystals.

The author wishes to acknowledge Prof. G. N. Ramachandran's help in suggesting the problem and for his valuable guidance during the course of the investigations.

Summary

The paper describes the study of the texture of crystals by using polarised X-rays. Some measurements on specimens of calcite and rocksalt are reported here and it is found that the relative intensities of various reflections and also the variation of the intensities of a particular reflection with the degree of perfection are broadly in agreement with the expectations from theory.

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SYNTHETICAL EXPERIMENTS IN THE CHROMONE GROUP

Part XXXI. A Synthesis of Muningin

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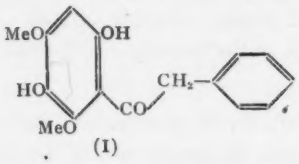
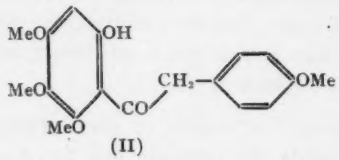
Received March 24, 1955

In connection with attempts to synthesize muningin (6:4′-dihydroxy-5:7-dimethoxyisoflavone)[1] we have reported[2] the synthesis of 6-hydroxy-5:7-dimethoxyisoflavone by the action of ethyl orthoformate on 2:5-dihydroxy-4:6-dimethoxyphenyl benzyl ketone (I). This ketone was prepared by



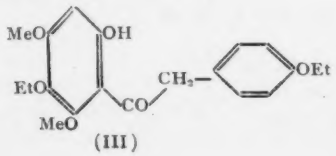
(I)



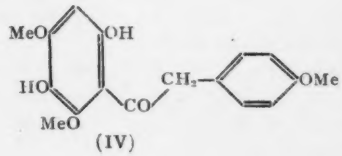
(II)

condensing 2:6-dimethoxyhydroquinone with the complex of phenylacetic acid and boron trifluoride, and was described as a yellow oil, b.p. 230–50°/1 mm. It has now been obtained as yellow prismatic needles, m.p. 108°, and the difficulty in crystallizing the substance has been traced to the presence of a small amount of the monophenylacetate, colourless needles, m.p. 105°. In subsequent preparations the ketone (I) was readily obtainable as yellow needles, m.p. 108°, by adding water and ether to the reaction mixture, extracting the ether-chloroform layer with aqueous caustic soda, acidifying the alkaline solution, ether-extracting, and crystallizing the residue after removal of the solvent. The ketone (I) was obtained in very poor yield by the persulphate oxidation of 2-hydroxy-4:6-dimethoxyphenyl benzyl ketone.

The acid-boron trifluoride complex method is of general use for the synthesis of phenolic ketones, and the ketones (II), (III) and (IV) have been prepared by this method.[3]

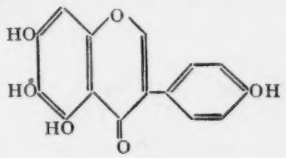


(III)

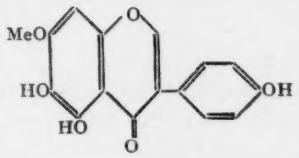


(IV)

The ketone (II) has been obtained earlier by the degradation of muningin dimethyl ether,[1] and by the interaction of antiarol, *p*-methoxyphenylacetyl chloride and aluminium chloride in ether.[4] The m.p. was quoted as 73° (King *et al.*[1]) and 96° (Krishnamurti and Seshadri[4]). The m.p. observed by us is 69°. Cyclization of (II) with ethyl orthoformate[5] gave 5:6:7:4′-tetramethoxyisoflavone (muningin dimethyl ether), m.p. 176°, the synthesis of which by the ethyl formate method has been reported earlier by Krishnamurti and Seshadri.[4] Demethylation with hydriodic acid gave 5:6:7:4′-tetrahydroxyisoflavone, m.p. 275° (*decomp.*) for the substance crystallizing with 1 H_2O. After sublimation at 0·2 mm. this isoflavone (V), which resembled baicalein and 5:6:7-trihydroxyisoflavone[2] in giving a flocculent bluish green precipitate by the addition of a drop of aqueous caustic soda to an alcoholic solution, melted at 280° (*decomp.*) and analysed for $C_{15}H_{10}O_6$, $2H_2O$. Muningin does not appear to have been demethylated



(V)



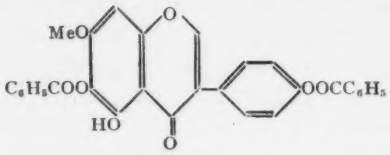
(VI)

to (V). The acetyl derivative, analysing correctly for a tetra-acetoxyisoflavone, melted at 205° (after shrinking at 197°) or 227° according as it was prepared from the crystallized or sublimed sample of (V). Methylation of (V), before or after sublimation, with potassium carbonate and dimethyl sulphate yielded the tetramethyl ether, m.p. 176°, from which (V) had been prepared by treatment with hydriodic acid.

When 5:6:7:4′-tetramethoxyisoflavone was heated with hydrobromic acid in acetic acid under specified conditions, the product was 5-hydroxy-6:7:4′-trimethoxyisoflavone, m.p. 186°, agreeing in its properties with the substance obtained by King *et al.*[1] by the selective methylation of 5:6:4′-trihydroxy-7-methoxyisoflavone (VI). We also isolated the same trimethyl ether in an attempt to monomethylate 5:6:7:4′-tetrahydroxyisoflavone (V).

Treatment of 5:6:7:4′-tetramethoxyisoflavone with hydriodic acid in acetic anhydride at 120° for 30 minutes yielded the monomethyl ether (VI), m.p. 263–64° (*decomp.*), the structure being assigned in view of the relative stability of the 7-methoxyl group.[6] With alkali it gave the Bargellini reaction, which is therefore not restricted to chromones containing hydroxyls in the 5:6:7-positions. Seshadri has recorded that herbacetin (3:5:7:8:4′-pentahydroxyflavone) responds to the Bargellini test.[7] King *et al.*[1] prepared

(VI) by the partial demethylation of muningin with hydrobromic acid in acetic acid, and they have recorded the m.p. 257° (*decomp.*). Benzoylation of (VI) with 2 mol. of benzoyl chloride in acetone in presence of potassium carbonate yielded the dibenzoate (VII). Methylation of (VII) by means



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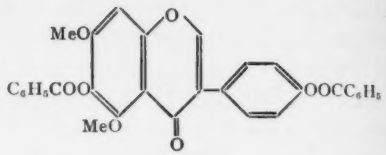
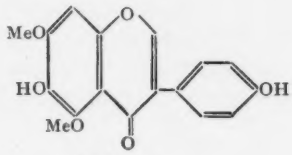


(VIII)



(IX)

of dimethyl sulphate and potassium carbonate in acetone gave 6: 4′-dibenzoyloxy-5: 7-dimethoxyisoflavone (VIII), m.p. 195°. The m.p. recorded by King[1] for the *O*-dibenzoyl derivative of natural muningin is 180°; but when natural muningin, kindly supplied by Professor F. E. King, was benzoylated by the acetone-potassium carbonate method, the product melted at 195°, not depressed by mixing with (VIII). The ester (VIII) was finally hydrolysed to muningin (IX) by shaking with 2% methanolic caustic potash (4 mol.) for about 1 hour at room temperature. The action of tosyl chloride (2 mol.) and potassium carbonate in acetone on (VI) gave a ditosylate, which was converted by methylation to 5: 7-dimethoxy-6: 4′-ditosyloxyisoflavone, m.p. 204°, identical with the *O*-ditosyl derivative prepared from muningin.

Ethyl orthoformate cyclization of the ketone (III) gave the corresponding isoflavone, m.p. 160°; the mixed m.p. with muningin diethyl ether, m.p. 153–56°, was 151–53°. Krishnamurti and Seshadri[8] have cited m.p. 156–58° for this isoflavone.

The ketone (IV) crystallized from hexane in yellow needles, m.p. 110°, and by the ethyl orthoformate method it yielded muningin 4′-methyl ether, m.p. 177°. The *O*-acetyl derivative melted at 213°.

EXPERIMENTAL

2-Hydroxy-4: 6-dimethoxy-5-phenylacetoxyphenyl benzyl ketone

The oily 2: 5-dihydroxy-4: 6-dimethoxyphenyl benzyl ketone described in an earlier paper[2] was dissolved in the minimum amount of hot absolute

alcohol and was left overnight at room temperature. After storage in a refrigerator for a few weeks, colourless needles separated. Recrystallization from dilute methyl or ethyl alcohol yielded colourless needles, m.p. 105° (Found: C, 71·0; H, 5·7. $C_{24}H_{22}O_6$ requires C, 70·9; H, 5·5%). The substance gives a reddish brown colouration with alcoholic ferric chloride.

2: 5-*Dihydroxy*-4: 6-*dimethoxyphenyl benzyl ketone* (I)

Method (*a*).—The above substance, m.p. 105°, was heated with 10% alcoholic potassium hydroxide for 2 hours on a water-bath. After dilution with water, removal of alcohol and acidification with concentrated hydrochloric acid, the solution was extracted with ether. Bicarbonate washings of the ether layer on acidification gave phenylacetic acid. The ether layer yielded an oil which crystallized from dilute alcohol in yellow prismatic needles, m.p. 108° (Found: C, 66·9; H, 5·8. $C_{16}H_{16}O_5$ requires C, 66·7; H, 5·6%). The mixed m.p. with the monophenylacetate described above was considerably depressed.

Method (*b*).—The condensation of phenylacetic acid (20 g.) and 2: 6-dimethoxyhydroquinone (5 g.) was carried out as described in an earlier paper.[2] The chloroform-ether layer was washed with sodium bicarbonate solution and then with aqueous caustic soda (500 ml.). The caustic soda extract was acidified with concentrated hydrochloric acid and then thoroughly extracted with ether. The oily residue from the ether layer solidified on keeping (7 g.) and crystallized from dilute alcohol in stout prismatic needles, m.p. 108°. No depression in the m.p. was observed when mixed with the substance obtained by method (*a*). The substance gives a green colour with ferric chloride, which immediately changes to yellow and finally to brownish red.

Method (*c*).—2-Hydroxy-4: 6-dimethoxyphenyl benzyl ketone (1·36 g.) was dissolved in pyridine (5 ml.), and caustic potash (1·4 g. in 14 ml. of water) was added. The solution was cooled to 10°, and treated with 5% aqueous potassium persulphate (25 ml.) during 3 hours with stirring. The reaction mixture was left overnight at room temperature, made acidic to Congo Red, the precipitate filtered and crystallized from dilute alcohol. The m.p. and mixed m.p. showed that this product was the starting material (0·3 g.). After extracting the filtrate with ether it was made strongly acidic with concentrated hydrochloric acid (20 ml.), heated on a boiling water-bath for 1 hour with the addition of a little sodium sulphite, cooled, and extracted with ether. The ether extract yielded an oil, which distilled at 220–40°/1 mm. (0·12 g.). When it was kept in contact with petroleum ether in a refrigerator for a long time, it crystallized in yellow needles, m.p. 108° (Found: C, 66·6; H, 5·6.

$C_{16}H_{16}O_5$ requires C, 66·7; H, 5·6%). The mixed m.p. with the ketone obtained by the boron trifluoride method showed no depression.

2-Hydroxy-4: 5: 6-trimethoxyphenyl 4'-methoxybenzyl ketone (II)

p-Methoxyphenylacetic acid (1·2 g.) was dissolved in dry alcohol-free chloroform (20 ml.) and the ice-cooled solution was saturated with boron trifluoride. To the red oily complex antiarol (0·6 g.) was added. The reaction mixture was left overnight at room temperature. Crushed ice was then added and the mixture extracted with ether. The ether-chloroform layer was washed with sodium bicarbonate solution and then with water, dried over anhydrous sodium sulphate, and the solvents distilled off. The residue was extracted with hexane and the insoluble portion proved to be antiarol. The hexane solution led to a pale yellow oil, which distilled at 210–20°/2 mm. (0·4 g.). When the oil was kept in contact with petroleum ether at − 5° for 2 days, it solidified, and then crystallized from the same solvent in colourless plates, m.p. 69° (King[1] and Seshadri[4] quote m.p.'s 73° and 96°) (Found: C, 65·2; H, 6·3. $C_{18}H_{20}O_6$ requires C, 65·1; H, 6·1%). The alcoholic solution gives a greenish brown colour with ferric chloride.

5: 6: 7: 4'-Tetramethoxyisoflavone

On the addition of ethyl orthoformate (5 ml.) and piperidine (10 drops) to a solution of the ketone (II) (2 g.) in pyridine (20 ml.) a pink colour developed, which turned to green, greenish yellow and finally yellowish brown when the solution was refluxed for 5 hours. The product obtained by treatment with ice and hydrochloric acid crystallized from methanol in colourless needles (1·4 g.), m.p. 176° (Found: C, 67·0; H, 5·6. $C_{19}H_{18}O_6$ requires C, 66·7; H, 5·3%) (King[1] and Seshadri[4] quote the same m.p.).

5-Hydroxy-6: 7: 4'-trimethoxyisoflavone

The above tetramethyl ether (0·5 g.) was heated with glacial acetic acid (2·5 ml.) and hydrobromic acid (b.p. 126°; 7·5 ml.) at 100°. As soon as crystals started separating from the clear solution, heating was discontinued, and the product was collected after cooling (0·42 g.). It crystallized from dilute acetic acid in colourless needles, m.p. 186° (King,[1] m.p. 186°) (Found: C, 66·2; H, 5·1. $C_{18}H_{16}O_6$ requires C, 65·9; H, 4·9%). The ferric colouration is green.

5: 6: 7: 4'-Tetrahydroxyisoflavone (V)

5: 6: 7: 4'-Tetramethoxyisoflavone (0·1 g.) was refluxed with acetic anhydride (1 ml.), acetic acid (1 ml.) and hydriodic acid (*d.* 1·7; 1 ml.) for 4 hours. After dilution with aqueous sodium bisulphite and cooling, the

product (70 mg.) was crystallized from dilute alcohol. The pale yellow needles had m.p. 275° (*decomp.*) (Found: in material dried at 130°/0·2 mm. for 2 hours: C, 59·4; H, 4·1. $C_{15}H_{10}O_6$, H_2O requires C, 59·2; H, 4·0%). The substance gives a deep green colour changing to greenish brown with alcoholic ferric chloride. A green colouration, followed by a bluish green precipitate, appears when a drop of aqueous caustic soda is added to an alcoholic solution of the substance. The *acetyl* derivative, prepared in the usual manner, crystallized from dilute acetic acid in colourless prisms m.p. 205°, with shrinking at 197° (Found: C, 61·0; H, 4·0. $C_{23}H_{18}O_{10}$ requires C, 60·7; H, 3·9%).

After sublimation at 0·2 mm. the m.p. of the tetrahydroxyisoflavone rose to 280° (*decomp.*) (Found: C, 56·3; H, 4·1. $C_{15}H_{10}O_6$, $2H_2O$ requires C, 55·9; H, 4·3%). The acetyl derivative crystallized from dilute acetic acid in colourless prisms, m.p. 227° (Found: C, 61·1; H, 4·1. $C_{23}H_{18}O_{10}$ requires C, 60·7; H, 3·9%). The mixed m.p. with the acetyl derivative, m.p. 205°, was 205° after shrinking at 197°. After prolonged storage the acetyl derivative, m.p. 227°, melted at 205° after shrinking at 197°.

On methylation of the tetrahydroxyisoflavone before or after sublimation with dimethyl sulphate and potassium carbonate in acetone, the parent tetramethoxyisoflavone, m.p. 176°, was obtained.

5:6:4′-*Trihydroxy-7-methoxyisoflavone* (*VI*)

5:6:7:4′-Tetramethoxyisoflavone (0·5 g.) was heated with acetic anhydride (5 ml.) and freshly distilled hydriodic acid (5 ml.) at 120° for half an hour. Worked up as usual, the product (0·4 g.) was boiled with water (200 ml.); the insoluble portion crystallized from glacial acetic acid in yellow prisms, m.p. 263–64° (*decomp.*) after shrinking at 258° (Found: C, 64·2; H, 4·1; OMe, 9·9. $C_{16}H_{12}O_6$ requires C, 64·0; H, 4·0; OMe, 10·3%). The m.p. quoted by King[1] is 257° (*decomp.*). The ferric reaction is green.

6:4′-*Dibenzoyloxy-5-hydroxy-7-methoxyisoflavone* (*VII*)

5:6:4′-Trihydroxy-7-methoxyisoflavone (VI) (0·6 g.) in boiling acetone (300 ml.) was treated with benzoyl chloride (2 mol., 0·46 ml.) and freshly ignited potassium carbonate (2 g.) during 3 hours. Potassium carbonate was filtered off and washed with hot acetone. Distillation of the acetone solution led to a greenish residue, which was refluxed with alcohol (Norit) and filtered. The filtrate was concentrated to a small volume and left at room temperature overnight. The colourless needles which separated (0·4 g.) melted at 185–86° (Found: C, 71·2; H, 4·2. $C_{30}H_{20}O_8$ requires

C, 70·9; H, 3·9%). An alcoholic solution of the substance gives a brown colour with ferric chloride.

6: 4′-Dibenzoyloxy-5: 7-dimethoxyisoflavone (VIII)

The above isoflavone (VII) (0·4 g.) in boiling acetone (200 ml.) was treated with potassium carbonate (2 g.) and dimethyl sulphate (0·5 ml.) for 6 hours. Acetone was recovered and water added to the residue. The precipitate was filtered and washed with water. It crystallized from alcohol in flat colourless needles, m.p. 195° (Found in material dried at 110°/1 mm.: C, 71·5; H, 4·5. $C_{31}H_{22}O_8$ requires C, 71·2; H, 4·2%). The substance is free from ferric reaction. When a sample of natural muningin was methylated similarly by the acetone-potassium carbonate method, the product crystallized from alcohol in flat colourless needles, m.p. 195°, not depressed by mixing with (VIII). King *et al.*[1] quote m.p. 180° for the *O*-dibenzoyl derivative of muningin prepared by means of benzoyl chloride and aqueous caustic soda.

Muningin (IX)

A suspension of 6: 4′-dibenzoyloxy-5: 7-dimethoxyisoflavone (VIII) (0·2 g.) in 2% methanolic caustic potash (5 ml.) was mechanically shaken at room temperature (30°) for 1 hour, when a clear yellow solution resulted. After dilution with water (10 c.c.) and acidification with concentrated hydrochloric acid, the colourless needles which separated were collected. As described by King for natural muningin,[1] synthetic muningin crystallized from dioxane in colourless minute hexagonal plates; the m.p. was 286° (*decomp.*) after shrinking at 280° and was not depressed by mixing with natural muningin (Found in material dried at 120°/1 mm.; C, 64·7; H, 4·8. $C_{17}H_{14}O_6$ requires C, 65·0; H, 4·5%). The substance gives no colouration with ferric chloride. It dissolves in concentrated sulphuric acid with a yellow colour, which turns deep red on the addition of a drop of concentrated nitric acid. It dissolves in aqueous sodium hydroxide with a yellow colour.

5-Hydroxy-7-methoxy-6: 4′-ditosyloxyisoflavone

The monomethyl ether (VI) (0·35 g.) in boiling acetone (150 ml.) was treated with *p*-toluenesulphonyl chloride (0·39 g. 2 mol.) and anhydrous potassium carbonate (1 g.) during 3 hours. On working up the product as described for the benzoyl analogue and crystallizing thrice from alcohol, pale brown prisms, m.p. 185°, were obtained (Found: C, 59·7; H, 4·2. $C_{30}H_{24}O_{10}S_2$ requires C, 59·2; H, 4·0%). An alcoholic solution of the substance gives a reddish brown colour with ferric chloride.

5: 7-*Dimethoxy*-6: 4′-*ditosyloxyisoflavone*

An acetone solution of the above isoflavone (0·1 g.) was refluxed for 18 hours with potassium carbonate (1 g.) and dimethyl sulphate (0·6 ml.). Acetone was removed by distillation, and water was added. The oily product solidified partly on leaving in a refrigerator, and crystallization from dilute acetic acid gave colourless prismatic needles, m.p. 204° (Found: C, 60·1; H, 4·2. $C_{31}H_{26}O_{10}S_2$ requires C, 59·8; H, 4·2%). The ditosylate prepared similarly from natural muningin had the same m.p. and mixed m.p.

2-*Hydroxy*-5-*ethoxy*-4: 6-*dimethoxyphenyl* 4-*ethoxybenzyl ketone* (*III*)

This ketone was prepared from *p*-ethoxyphenylacetic acid (1·2 g.) and 4-ethoxy-3: 5-dimethoxyphenol (0·6 g.) by the procedure described for the ketone (II). The yellow oil distilled at 220–30°/0·5 mm. (0·34 g.), and crystallized from ethyl acetate with great difficulty in colourless plates, m.p. 104° (Krishnamurti and Seshadri,[8] m.p. 104°) (Found: C, 66·3; H, 7·1. $C_{20}H_{24}O_6$ requires C, 66·7; H, 6·7%). The ferric colouration is red-brown.

6: 4′-*Diethoxy*-5: 7-*dimethoxyisoflavone*

The orange solution of the above ketone (0·15 g.) in pyridine (2 ml.), ethyl orthoformate (1 ml.) and piperidine (2 drops) changed to brown on heating. After refluxing for 5 hours and adding to ice and hydrochloric acid, the product (0·11 g.) was collected and crystallized from alcohol. The colourless needles had m.p. 160°. The mixed m.p. with a sample of *O*-diethyl muningin, which melted at 153–56°, was 151–53° (Found: C, 68·2; H, 6·2. $C_{21}H_{22}O_6$ requires C, 68·1; H, 6·0%).

2: 5-*Dihydroxy*-4: 6-*dimethoxyphenyl* 4-*methoxybenzyl ketone* (*IV*)

Using *p*-methoxyphenylacetic acid (10 g.) and 2: 6-dimethoxyhydroquinone (4 g.) and following the same procedure as for the ketone (II), the ether-chloroform layer was washed with sodium bicarbonate solution, from which *p*-methoxyphenylacetic acid (8 g.) was recovered. Aqueous sodium carbonate extraction led to an unworkable sticky brownish product. Final extraction with 10% caustic soda solution, acidification and ether extraction yielded a reddish viscous oil (2·7 g.). Extraction of this oil with hexane gave a crystalline substance (0·7 g.), part of which was soluble in aqueous sodium bicarbonate. Acidification of the solution gave *p*-methoxyphenylacetic acid, resulting apparently from the hydrolysis of the mono-*p*-methoxyphenylacetate of the desired ketone (IV) by the action of aqueous caustic soda. This ester could not be isolated in crystalline form. The bicarbonate-insoluble substance crystallized from hexane in yellow prismatic needles (0·1 g.), m.p. 110° (Found: C, 64·5; H, 5·7. $C_{17}H_{18}O_6$ requires C, 64·1;

H, 5·7%). On the addition of alcoholic ferric chloride an alcoholic solution of the substance turns green, then yellow and red.

6-Hydroxy-5: 7: 4′-trimethoxyisoflavone

The ketone (IV) (50 mg.) was refluxed with pyridine (1 ml.), ethyl orthoformate (0·5 ml.) and piperidine (2 drops) for 5 hours. The isoflavone was isolated by adding ice and hydrochloric acid and extracting with ether, and it crystallized from dilute alcohol in colourless needles (20 mg.), m.p. 177° (Found: C, 66·7; H, 5·2. $C_{18}H_{16}O_6$ requires C, 65·9; H, 4·9%). The substance has no ferric reaction. The *acetyl* derivative crystallized from dilute alcohol in colourless needles, m.p. 213° (Found: C, 64·8; H, 4·9. $C_{20}H_{18}O_7$ requires C, 64·9; H, 4·8%).

p-*Methoxyphenylacetic acid*

A solution of *p*-methoxyphenylpyruvic acid[9] (5 g.) in 10% aqueous caustic soda (30 c.c.), cooled to 0°, was treated with 3% hydrogen peroxide (30 c.c.) gradually (*cf.* Robinson and Young[10]). Acidification after 12 hours gave *p*-methoxyphenylacetic acid, which crystallized from water in colourless plates (3·8 g.), m.p. 84–85°.

p-*Ethoxyphenylacetic acid*

This was also prepared by the oxidation of *p*-ethoxyphenylpyruvic acid[11] with 3% hydrogen peroxide.[10]

SUMMARY

2: 5-Dihydroxy-4: 6-dimethoxyphenyl benzyl ketone (I) described earlier as a yellow oil, b.p. 230–50°/1 mm., has now been obtained as yellow prismatic needles, m.p. 108°. The acid-boron trifluoride complex method is of general use for the synthesis of phenolic ketones; 2-hydroxy-4: 5: 6-trimethoxyphenyl 4-methoxybenzyl ketone (II), 2-hydroxy-5-ethoxy-4: 6-dimethoxyphenyl 4-ethoxybenzyl ketone (III) and 2: 5-dihydroxy-4: 6-dimethoxyphenyl 4-methoxybenzyl ketone (IV) have thus been prepared. The cyclization of (II) with ethyl orthoformate gave 5: 6: 7: 4′-tetramethoxyisoflavone, which was then demethylated to 5: 6: 7: 4′-tetrahydroxyisoflavone (V). Partial demethylation of 5: 6: 7: 4′-tetramethoxyisoflavone to 5-hydroxy-6: 7: 4′-trimethoxyisoflavone and 5: 6: 4′-trihydroxy-7-methoxyisoflavone (VI) has been effected.

Treatment of (VI) in acetone with benzoyl chloride (2 mol.) and potassium carbonate gave 6: 4′-dibenzoyloxy-5-hydroxy-7-methoxyisoflavone (VII), methylation of which yielded 6: 4′-dibenzoyloxy-5: 7-dimethoxyisoflavone (VIII). The m.p. of (VIII) was not depressed by mixing with the dibenzoyl

derivative prepared from natural muningin by means of benzoyl chloride and potassium carbonate in acetone. Hydrolysis of (VIII) with 2% methanolic caustic potash at 30° and acidification gave 6 : 4′-dihydroxy-5 : 7-dimethoxy-isoflavone, identical with natural muningin. The ditosyl analogues of (VII) and (VIII) were similarly prepared.

Ethyl orthoformate cyclization of the ketone (III) gave muningin diethyl ether, and cyclization of the ketone (IV) yielded muningin 4′-methyl ether.

Acknowledgment

We are greatly indebted to Professor F. E. King, F.R.S., for samples of muningin and its diethyl ether, and to Dr. T. S. Gore for the microanalyse recorded in the paper.

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STRAGGLING OF THE RANGE OF FAST PARTICLES AS A STOCHASTIC PROCESS*

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Received March 10, 1955

Statement of the Problem

We shall adopt the following stochastic model to represent the well-known phenomenon of straggling of the range of fast particles in passing through matter.

Considering only one-dimensional penetration of matter by fast particles we assume that a particle of energy E at t (t being the thickness of matter traversed) loses energy in two ways:—

1. Deterministically by an amount $\beta(E)\,dt$ in passing through matter of thickness dt. Such a loss is attributed to ionisation of the atoms of matter.

2. By the random process of radiation of photons (Bremmstrahlung). A particle of energy E drops to an energy interval $(E', E' + dE')$ by radiating a photon of energy $E - E'$ in passing through matter of thickness dt with probability $R(E'|E)\,dE'\,dt$.

We now define absorption in the following manner. If a particle drops to an energy below a critical energy E_c between t and $t + dt$, we say it is absorbed and its range lies between t and $t + dt$. Our problem is to determine the probability distribution of the range, given the initial energy (*i.e.*, at $t = 0$) of the particle.

Formal Solution of the Problem

The first step is to write the stochastic equation for the probability $\pi(E|E_0;\ t)\,dE$ of the energy of the particle having a value between E and $E + dE$ at t, given that the initial energy was E_0. This has been already done by the authors in an earlier contribution to these *Proceedings* (1953). The equation is

$$\frac{\partial \pi(E|E_0;\ t)}{\partial t} = -\pi(E|E_0;\ t)\int_0^E R(E'|E)\,dE' + \int_E^{E_0} \pi(E'|E_0;\ t)\,R(E|E')\,dE'. \tag{1}$$

* Read at the Annual Meeting of the Indian Academy of Sciences at Belgaum in December 1954.

Using our definition of absorption we find that the probability that the particle is absorbed within a distance t can be formally written as

$$P(E_c;\ t) = \int_0^{E_c} \pi(E|\ E_0;\ t)\, dE = 1 - \int_{E_c}^{E_0} \pi(E|\ E_0;\ t)\, dE \qquad (2)$$

and it immediately follows that the probability that the particle is absorbed between t and $t + dt$ is $\frac{\partial P(E_c;t)}{\partial t}\, dt$ *i.e.*, $\frac{\partial P\ (E_c;\ t)}{\partial t}$ is the probability frequency function of the range of the particle.

To proceed further and obtain the explicit solution of equation (1) and to determine the distribution of the range, it is necessary to make simplifying assumptions regarding the form of the cross-section $R(E'|\ E)$ and of the function $\beta(E)$. In the case when $R(E'|\ E)\, dE'$ can be expressed as $R(q)\, dq$, $(q = E'|E)$ and $\beta(E)$ is of the form βE^k, equation (1) has been reduced to a difference-differential equation by the application of the Mellin's transform technique. However the solution of the transform equation is still difficult and therefore the authors made the further assumptions that $R(q') = \delta(q' - q)$, δ being the Dirac delta function, and $\beta(E) = \beta$, a constant for $E > 0$ and $\beta(E) = 0$ for $E = 0$. $p(s;\ t)$, the Mellin's transform of π satisfies the equation

$$\frac{\partial p(s;\ t)}{\partial t} = -\alpha\, p(s;\ t) + \omega(s)\, p(s;\ t) + \beta(s-1)\, p(s-1;\ t) \qquad (3)$$

where

$$\alpha = \int_0^1 R(q)\, dq,\ \omega(s) = \int_0^1 R(q)\, q^{s-1}\, dq$$

The solution of this equation was obtained earlier by the authors by an indirect procedure. The equation with a negative sign for the last term on the right was first solved, since in this case the stochastic variate cannot assume the value zero and therefore no complication due to the delta function singularity at zero energy arises. This result was used to obtain the solution for equation (1) (see Ramakrishnan and Mathews, 1953). However Srinivasan** has shown recently that the solution of the integro-differential equation for π may be obtained directly if a Laplace transformation instead of Mellin's is employed, though it would appear to be unsuitable at first sight. The solution for π is

$$\pi(E|\ E_0;\ t) = \sum_{n=0}^{\infty} \pi_n(E|\ E_0;\ t) \qquad (4)$$

** Private communication. A brief outline of his derivation is given in the Appendix.

where

$$\pi_0(\mathrm{E}|\,\mathrm{E}_0;\ t) = e^{-\alpha t}\delta(\mathrm{E} - \mathrm{E}_0 + t)$$

and

$$\pi_n(\mathrm{E}|\,\mathrm{E}_0;\ t) = -\frac{\alpha^n e^{-\alpha t}}{(n-1)!}\sum_{k=0}^{m-1} \mathrm{A}_k{}^n (\mathrm{E}_0 q^n - \mathrm{E} - tq^k)^{n-1},$$

$$n \geqslant 1,\ \mathrm{E} > 0,\ tq^m < \mathrm{E}_0 q^n - \mathrm{E} < tq^{m-1}. \tag{5}$$

We have put β equal to unity without loss of generality by suitably choosing the unit of E and $\mathrm{A}_k{}^n$ is given by

$$\mathrm{A}_k{}^n = \prod_{\substack{j=0 \\ j\neq k}}^{n} (q^j - q^k)^{-1} \tag{6}$$

Since we have assumed β to be independent of E for $\mathrm{E} > 0$, it is clear from the very nature of the problem that there is a finite probability of the particle having an energy exactly equal to zero [*i.e.*, there exists a delta function singularity for $\pi\ (\mathrm{E}|\,\mathrm{E}_0;\ t)$ at $\mathrm{E} = 0$], and this is the probability that the particle is absorbed, provided we consider absorption to take place as soon as the energy is reduced to zero‡. This probability has been shown to be

$$\mathrm{P}\ (0;\ t)\ = \sum_{n=0}^{\infty} \mathrm{P}\,(0,\ n;\ t),$$

$$\mathrm{P}\,(0,\ 0;\ t) = e^{-t}\ \mathrm{H}\ (t - \mathrm{E}_0)$$

$$\mathrm{P}\,(0,\ n;\ t) = \frac{e^{-t}\,t^n}{n!}\sum_{k=0}^{r-1} \mathrm{A}_k{}^n\ (q^n\,\mathrm{E}_0/t - q^k)^n,\ \ (tq^r < \mathrm{E}_0 q^n < tq^{r-1}) \tag{7}$$

where α also has been put equal to unity by a proper choice of the unit of t.

Numerical evaluation of this expression has been done for various values of the initial energy E_0, with $q = \frac{1}{2}$. In the energy loss of fast electrons, the fraction of energy lost by the electron in each radiative collision is usually between $\frac{1}{3}$ and $\frac{2}{3}$ (see for example, Heitler, 1943). So the value we have chosen corresponds fairly to physical facts. The results are tabulated below and also illustrated in a graph.

‡ It is necessary to assume a non-zero value for E_0 if the mechanism of energy loss is such that the energy of the particle approaches zero only asymptotically, for example when $\beta(\mathrm{E})$ is of the form $\beta\mathrm{E}^k$, $k > 0$. But in our model the constant rate of loss causes the energy to drop to zero within a distance E_0/β, and so the range can be defined as the distance in which the energy drops to zero.

TABLE I

P (0, *t*)

E_0 / *t*	5	10	20	50	100	500	1000	10000
1	·024	·003						
2	·381	·139	·038	·005	·001			
3	·814	·489	·232	·066	·021	·001		
4	·960	·784	·523	·232	·106	·011	·003	
5		·924	·757	·463	·271	·050	·020	·001
6		·980	·894	·673	·474	·137	·068	·004
8		·999	·985	·912	·799	·433	·289	·044
10			·998	·982	·944	·724	·585	·181

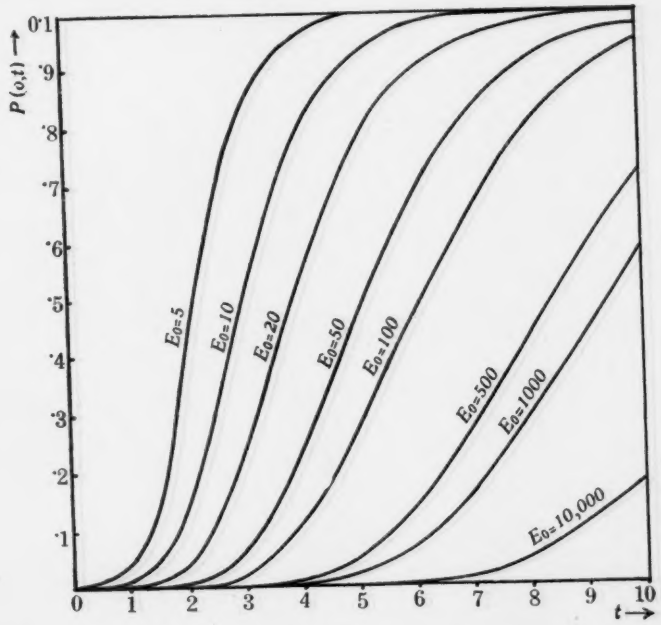

Fig. 1. P (0; *t*), the probability that the particle has been absorbed between 0 and *t*.

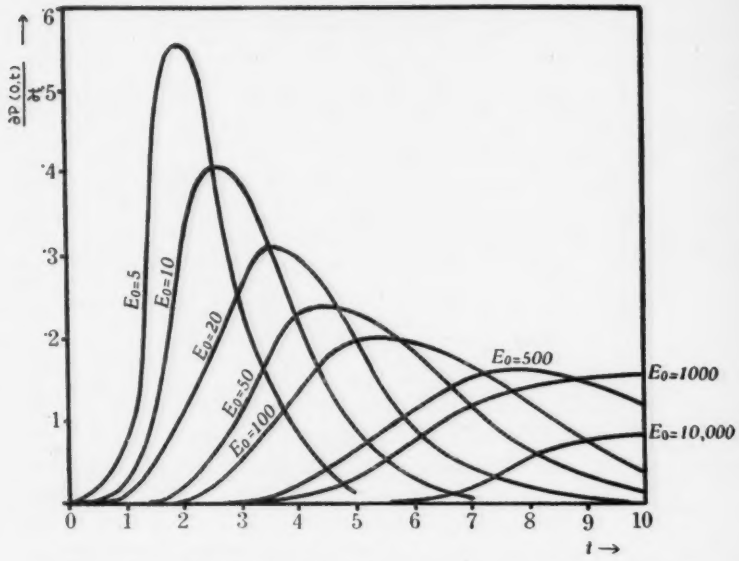

Fig. 2. $\partial P(0; t)/dt$, the probability frequency function of the range t.

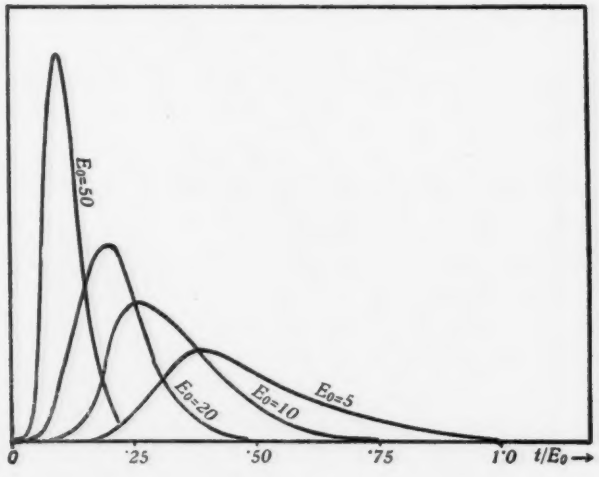

Fig. 3. The probability frequency function of the random variable t/E_0, t being the range.

The probability frequency function of the range, as mentioned before, is $\partial P/\partial t$ and the moments of the range R of the particle are given by

$$\epsilon \{R^r\} = \int_0^{E_0} t^r \frac{\partial P}{\partial t}\, dt, \quad r = 1, 2, \ldots. \tag{8}$$

We have not computed any of the moments, as the distribution itself is known.§ The graph of $\partial P/\partial t$, obtained by graphical differentiation of the $P - t$ curves is given to show the form of the range distribution. If $\partial P/\partial t$ is directly plotted against t, the curve for a given initial value of the energy E_0 extends from $t = 0$ to $t = E_0$, and the curves for the larger values of E_0 appear to be flatter than those for small values. But a plot of the distribution of t/E_0 gives a much better idea of the sharpness of the distribution. It is clearly seen that the distribution rapidly becomes sharp for increasing values of the initial energy E_0. One feature that is easily noticed from the curves is that the mean range $\bar{R}$ does not increase in proportion to the energy. In fact, $\bar{R}/E_0$ decreases as E_0 increases.

Janossy's Simple Alternative Stochastic Model of Straggling

It is interesting to compare our model with a simpler alternative model discussed by Janossy (1950) in his book on *Cosmic Rays*.

A particle undergoes a collision with probability αdt in traversing material of thickness dt and loses energy of magnitude ϵ per collision. Thus if E_0 is its initial energy, it is absorbed if it undergoes N collisions where N is an integer such that $(N - 1)\,\epsilon < E_0 \leqslant N\epsilon$. The probability that the Nth collision occurs between t and $t + dt$ is given by the Poisson law.

$$P(N;\ t)\, dt = e^{-\alpha t} \frac{(\alpha t)^{N-1}}{(N-1)!}\, \alpha dt \tag{9}$$

and this is the distribution of the range. It is interesting to note that for very large N the distribution tends to a Gaussian one with respect to t in the neighbourhood of the maximum which is very sharp and occurs at $t=(N-1)/\alpha$.

Normally, when we speak of a Gaussian approximation to a Poisson distribution we mean that $e^{-\alpha t}(\alpha t)^N/N\,!$ assumes a Gaussian form with respect to N if αt is very large. Here in (9) we are speaking of a distribution

§ Usually in stochastic problems the expressions for the first few moments are easily obtained in simple form, while the frequency function itself may be very complicated. In such cases, the moments are computed to get an approximate idea of the distribution. But the present case is among the few where the expressions for the moments are no simpler than the expression for the frequency function.

with respect to t and hence it seems worthwhile to indicate the derivation of the asymptotic Gaussian form for large N.

Putting at

$$at = N - 1 + a\tau$$

we have

$$\frac{e^{-at}(at)^{N-1}}{(N-1)!} = e^{-(N-1)}\frac{(N-1)^{N-1}}{(N-1)!}\left(1 + \frac{a\tau}{N-1}\right)^{N-1} e^{-a\tau} \tag{10}$$

We immediately note that for large N,

$$\frac{e^{-(N-1)}(N-1)^{N-1}}{(N-1)!} \sim \frac{1}{\sqrt{2\pi(N-1)}}$$

and

$$e^{-a\tau}\left(1 + \frac{a\tau}{N-1}\right)^{N-1} \sim e^{-(a\tau)^2/2(N-1)}$$

in the region $a\tau << N$. When $a\tau$ is comparable to $N - 1$ (10) becomes vanishingly small. Thus (9) tends to a Gaussian distribution with the mean $(N - 1)/a$.

APPENDIX

In a private communication, S. K. Srinivasan has shown that it is possible to obtain $\pi(\mathrm{E}|\,\mathrm{E}_0;\ t)$ directly by applying a Laplace transformation to the differential equation satisfied by $\pi_n(\mathrm{E}|\,\mathrm{E}_0;\ t)$ where $\pi_n\ (\mathrm{E}|\,\mathrm{E}_0;\ t)\ d\mathrm{E}$ is the joint probability that the particle has undergone n radiative collisions in the interval $(0,\ t)$ and its energy is between E and $\mathrm{E}+d\mathrm{E}$ at t. The equation for π_n is

$$\frac{\partial \pi_n(\mathrm{E};\ t)}{\partial t} = -\ a\pi_n(\mathrm{E};\ t) + \frac{a}{q}\pi_{n-1}\left(\frac{\mathrm{E}}{q};\ t\right) + \frac{\partial}{\partial \mathrm{E}}\{\beta(\mathrm{E})\,\pi_n(\mathrm{E};\ t)\} \quad (11)$$

with $\beta(\mathrm{E}) = \beta = 1$ for $\mathrm{E} > 0$ and $\beta(\mathrm{E}) = 0$ for $\mathrm{E} = 0$,

and

$$\pi_0(\mathrm{E};\ t) = e^{-at}\ \delta(\mathrm{E} - \mathrm{E}_0 + t).$$

A Laplace transformation now yields

$$\frac{\partial p_n(s;\ t)}{\partial t} = -\ ap_n(s;\ t) + ap_{n-1}(sq;\ t) + s\,p_n(s;\ t) \quad (12)$$

when it is borne in mind that $\beta(\mathrm{E}) = 0$ at $\mathrm{E} = 0$, so that the term $[\beta(\mathrm{E})\,\pi_n(\mathrm{E};\ t)e^{-s\mathrm{E}}]_{\mathrm{E}=0}$ which occurs in the Laplace transform of the last term of equation (11) vanishes. It is interesting to note that it is this peculiar feature of the function $\beta(\mathrm{E})$ that renders the solution possible. Otherwise this extra term introduces complications which cannot easily be resolved.

A further Laplace Transform with respect to t reduces the equation to a simple iterative relation

$$\rho_n(s;\ r) = \frac{a}{a - s + r}\ \rho_{n-1}(sq;\ r) \quad (13)$$

which immediately gives

$$\rho_n(s;\ r) = a^n\, e^{-\mathrm{SE}_0 q^n} \prod_{k=0}^{n} \frac{1}{a + r - sq^k} \quad (14)$$

The solution for π can be obtained from this at once by inversion.

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STEREOCHEMISTRY OF 3-HYDROXY FLAVANONES*

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Received April 15, 1955

A number of 3-hydroxy flavanones (flavanolones) (I) have been isolated from natural sources and several have been obtained synthetically by methods enumerated below:—

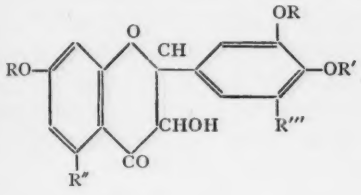
(1) *Reduction of the corresponding flavonol* (*II*).—The preparation of dihydroquercetin (I *b*) and dihydrokæmpferol (IV *c*) by this method using alkaline sodium hydrosulphite was carried out by Pew[1] and dihydromyricetin (I *d*) by Kotake, Kubota and Ichikawa.[2] The method was improved by Geissman and Lischner[3] and Shimizu and Yoshikawa.[4] Geissman *et al.*, also obtained small quantities of 2-hydroxy-2-benzyl coumaranones as by-products.

(2) *Ring closure starting from chalkones* (*III*).—Murakami and Irie[5] first used for this purpose alkaline hydrogen peroxide under controlled conditions. A detailed study of this reaction was made later by Reichel and Steudel[6] and more recently by Guider, Simpson and Thomas[7]. Oyamada[8] converted 2-acetoxy-4: 3′: 4′-trimethoxy chalkone (III) *via* its dibromide, diacetate and subsequent hydrolysis to fustin trimethyl ether (I *c*). More recently Marathe, Chandorkar and Limaye[9] have shown that chalkone dibromides yield 3-hydroxy flavanones (I) by heating with aqueous acetone and sodium carbonate.

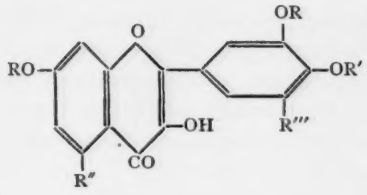
(3) *Substitution in the* 3*-position of flavanones* (*IV*).—In the earliest method of Zemplen and Bognar[10] bromination in the 3-position was effected in the presence of ultra-violet light, and the bromine atom replaced in two steps by a hydroxyl. Cavill *et al.*[14] applied this method to 7-methoxy flavanone and obtained only the flavone at the end. During the course of the present work when 3-bromo naringenin triacetate (IV *f*) was boiled with acetic anhydride and silver acetate it yielded apigenin acetate (V *h*) as the major product and dihydrokæmpferol tetra-acetate (IV *d*) as the minor product. It would appear that a mixture of flavone and flavanolone are generally produced, the proportions varying with conditions and in earlier work only the major

* Naturally occurring 3-hydroxy flavanones are specified by their trivial names and the synthetic ones by the method of preparation.

product might have been isolated after purification. Goel, Narasimhachari and Seshadri[11] employed iodine and silver acetate in absolute alcohol whereby in several cases the 3-acetoxy flavanones were produced. The action of lead tetra-acetate on flavanones has been observed by a number of workers.[12-14] to give a small yield of 3-acetoxy flavanones along with flavones and isoflavones. More recently Mahesh and Seshadri[15] have found that the action of Fenton's reagent on flavanone acetates (IV *h*) provides a convenient method for hydroxylation in the 3-position. This and the iodine-silver acetate method of Goel *et al.*[11] seem to effect simple substitution and are therefore considered to be typical examples.

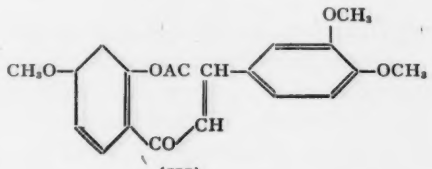


(I)



(II)

a R=R'=R''=R'''=H
b R=R'=R'''=H; R''=OH
c R=R'=CH_3; R''=R'''=H
d R=R'=H; R''=R'''=OH
e R=R'=CH_3; R''=R'''=OCH_3
f R=R'''=H; R'=CH_3; R''=OH



(III)

There seemed to exist appreciable differences between various samples of 3-hydroxy flavanones (I) obtained from natural sources and by different synthetic methods. These should be capable of explanation based on the stereochemistry of these structures. Among their transformations (*a*) dehydrogenation and (*b*) dehydration are the most important. The former gives rise to flavonols while the latter gives flavones.

(*a*) A number of methods have been used for dehydrogenation.

(i) *Catalytic.*—Kotake and Kubota[16] heated ampelopsin (I *d*) with cinnamic acid in the presence of P*d*-charcoal at 170° and obtained myricetin (II *d*). Later Lindstedt[17] used this method for the dehydrogenation of pinobanksin (IV *a*).

(ii) *Oxidation in alkaline solution.*—Murakamiand Irie[5] first showed that 3-hydroxy flavanones (I) obtained by synthetic method (2) underwent dehydrogenation to flavonols (II) with alkaline hydrogen peroxide. In the course of the present work using this reagent pinobanksin (IV *a*) obtained from the wood of *Pinus excelsa* has been dehydrogenated to galangin (V*a*). Oyamada[18] showed that fustin (I *a*) underwent similar oxidation in alkali in presence of air to yield fisetin (II *a*). These two processes have been applied to a number of synthetic (Method 2) dihydroflavonols also by Reichel and Steudel.[6]

(iii) *Disproportionation.*—Marathe *et al.*[9] have reported dehydrogenation by disproportionation on heating simple dihydroflavonol [synthetic method (2)] with alcoholic sodium hydroxide in absence of air or by simple thermal disproportionation. It has also been observed by Cavill *et al.*[14] that 3-acetoxy flavanones prepared by the action of lead tetra-acetate on flavanones undergo hydrolysis accompanied by dehydrogenation when treated with alcoholic NH_3 at 0°.

It may be noted that in alkaline solutions the opening of the pyranone ring is an important feature and may be responsible for by-products such as 2-hydroxy-2-benzyl coumaran-3-ones,[19, 20] 3-benzal coumaran-2-ones,[9, 19, 21] 2-benzyl[22] and 2-benzal[23, 24] coumaran-3-ones.

(iv) *During methylation.*—Kubota[25] observed that the use of aqueous alkali and methyl sulphate converted ampelopsin pentamethyl ether (I *e*) into myricetin hexamethyl ether. A similar observation was made by Lindstedt[17] and Goel *et al.*[11] using methyl sulphate and anhydrous potassium carbonate in acetone solution. The former showed that pinobanksin (IV *a*) first yielded its dimethyl (IV *g*) ether which finally changed into galangin trimethyl ether (V *i*) in small yields. The latter reported similar results with 3-hydroxy naringenin (IV *c*) natural as well as synthetic [method (3)]. The dehydrogenation could be brought about even by simply boiling with acetone and potassium carbonate.[11]

(v) *Bismuth acetate.*—More recently Guider *et al.*[7] have used bismuth acetate for the conversion of synthetic 3-hydroxy flavanones (I) obtained by method (2) into flavonols (II). This reagent is specific for the oxidation of $-CHOH$ to $-CO$ and is considered to function here in this manner. In the course of the present work it has been used to oxidise taxifolin (I *b*) and 3-hydroxy naringenin (IV *c*) prepared by Fenton's oxidation and is found to work very satisfactorily. Other methods of dehydrogenation are discussed later.

(*b*) *Dehydration.*—By boiling with acetic anhydride the natural as well as synthetic flavanolones (I) made by method (3) undergo dehydration yielding the corresponding flavone acetates (V *h*) though the yields are variable. In general the natural samples give much poorer yields.

The methods discussed above are not of value for the study of the stereochemistry of the 3-hydroxy flavanones since the use of high temperatures and strong reagents are involved and the use of alkali also opens the pyranone ring. The results yielded by the following methods seem to be, however, significant since they represent mild treatments.

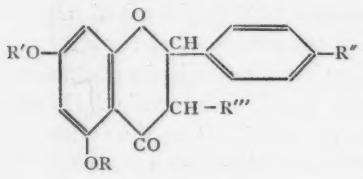
(i) *Dilute sulphuric acid in the presence of air.*—Pew[1] observed dehydrogenation of taxifolin (I *b*) by this method giving good yields of quercetin (II *b*). Cavill *et al.*[14] report that 3-hydroxy flavanones (I) obtained by lead tetracetate method behave in a similar way. During the course of the present work a similar observation has been made using a sample of dihydroquercetin (I *b*) prepared by method (1), dihydrorhamnocitrin (IV *e*) by method (2) and 3-hydroxy naringenin (IV *c*) by Zemplen's method. On the other hand Goel *et al.*[11] observed that under this treatment 3-hydroxy naringenin (IV *c*) prepared by the iodine-silver acetate method undergoes dehydration to apigenin (V *b*); Fenton's oxidation products also are now found to suffer dehydration in the same way.

(ii) *Iodine oxidation.*—Iodine in the presence of alcoholic sodium acetate has been employed earlier by Narasimhachari and Seshadri[26] for the conversion of flavanones (IV *b*) into flavones (V *b*). Its action on 3-hydroxy flavanones has now been studied. Pinobanksin (IV *a*), pinobanksin-7-methyl ether (IV *j*), aromadendrin (IV *c*), taxifolin (I *b*) and dihydroquercetin (I *b*) prepared by method (1) are found to undergo smooth dehydrogenation to give good yields of galangin (V *a*), izalpinin (V *j*), kæmpferol (V *c*) and quercetin (II *b*) respectively. A sample of 3-hydroxy naringenin (IV *c*) obtained by synthetic method (3), however, behaves differently and yields small amounts of kæmpferol (V *c*) along with a major yield of an iodo compound, and a considerable portion of the original substance is recovered which could be made to react again to yield more of the iodo compound but not kæmpferol (V *c*). The iodo compound decomposes rather readily and when refluxed with pyridine yields kæmpferol (V *c*). A sample of 3-hydroxy hesperetin (I *f*) prepared by the same synthetic method gave similar results.

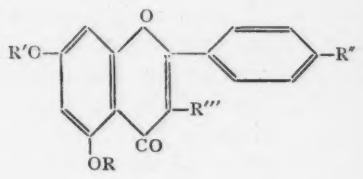
A similar though somewhat different result has been obtained using boiling glacial acetic acid and fused potassium acetate instead of alcohol for this reaction. Slightly better yields of quercetin (II *b*) are obtained from taxi-

folin (I *b*). In the case of synthetic 3-hydroxy naringenin (IV *c*) obtained by method (3) the yield of kæmpferol (V *c*) and the iodo compound was higher and there was no recovery of unchanged material.

In view of the peculiar behaviour of these synthetic compounds the action of 4% alcoholic sulphuric acid on 3-hydroxy naringenin (IV *c*) obtained by method (3) has been reinvestigated. The major product was apigenin (V *b*) and could be readily obtained pure by crystallisation from alcohol. When the mother liquor was subjected to circular paper chromatography two rings corresponding to those of kæmpferol (V *c*) (weak) and apigenin (V *b*) (strong) were obtained. The behaviour of these samples will be discussed in detail later on.



(IV)



(V)

a R = R′ = R″ = H; R‴ = OH
b R = R′ = R‴ = H; R″ = OH
c R = R′ = H; R″ = R‴ = OH
d R = R′ = Ac; R″ = R‴ = OAc
e R = H; R′ = CH_3; R″ = R‴ = OH
f R = R′ = Ac; R″ = OAc; R‴ = Br
g R = R′ = CH_3; R″ = H; R‴ = OH
h R = R′ = Ac; R″ = OAc; R‴ = H
i R = R′ = CH_3; R″ = H; R‴ = OCH_3
j R = R″ = H; R′ = CH_3; R‴ = OH

An explanation of the above observations could be sought from a study of the conformation of the simple flavanone and 3-hydroxy flavanone structures. In molecular models of flavanones, carbon atoms 2 and 3 of the pyranone ring (A, see Formula VI) are not in the same plane as the other atoms of this ring and of the condensed benzene ring, though the deviation is not much. Of the non-ring bonds of each of these two carbon atoms, one is axial and the other is equatorial. The equatorial bonds are *cis* to each other. There are two ways in which the axial bonds could be arranged (i) axial bond in the 2-position (α,....) and axial bond in the 3-position (β,___) (VI *a*) and (ii) the reverse (VII *a*). These would represent mirror-image forms. In the case of simple flavanones the 2-phenyl should be allotted the equatorial bond by virtue of its bulk; consequently the C_2-hydrogen should be axial and the bond can be α or β representing the (+) or (−) form. A number of optically active flavanones are now known and they are mostly (−) in rotation.

3-HYDROXY FLAVANONES

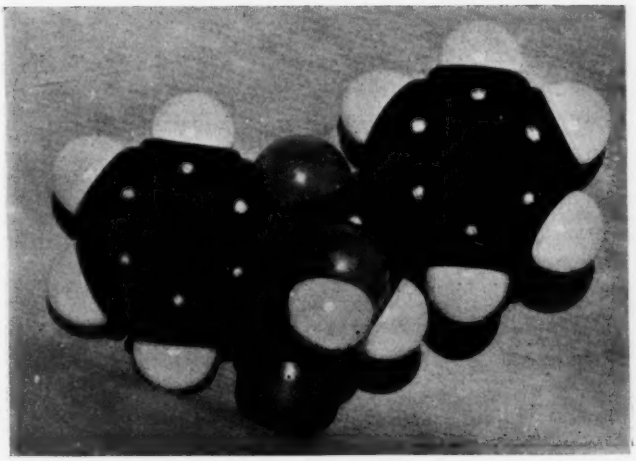


FIG. 1. Front view.

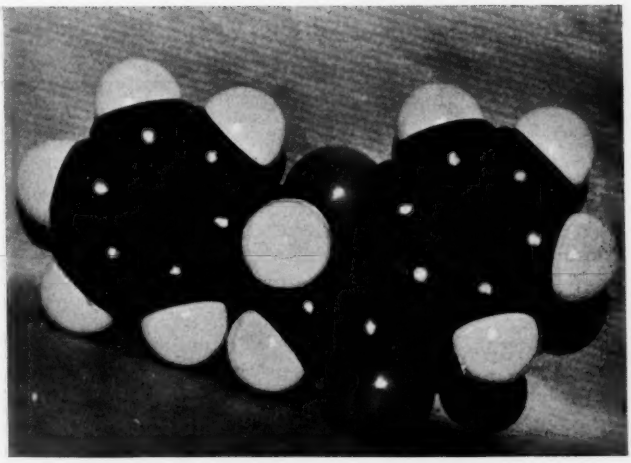


FIG. 2. Back view.

FIGS. 1 and 2. Side phenyl in the 2-position and hydrogen atom in the 3-position are equatorial. Axial hydrogen in the 2-position (Fig. 2) and axial hydroxyl in the 3-position (Fig. 1) are visible.

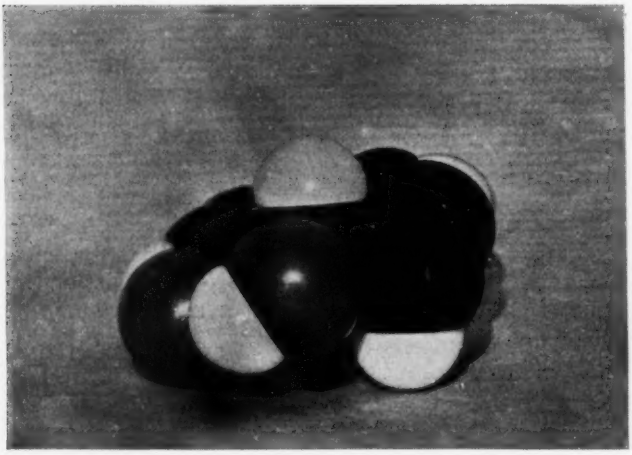


FIG. 3. Side view: side phenyl omitted.

FIG. 3. Hydrogen atoms in 2 and 3-positions are axial and trans while hydroxyl in the 3-position is equatorial.

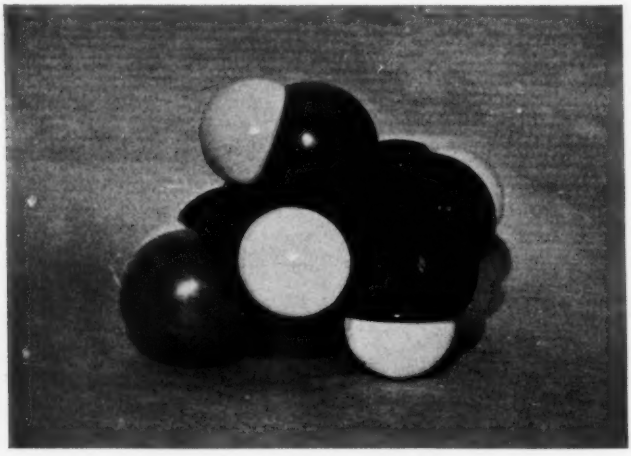
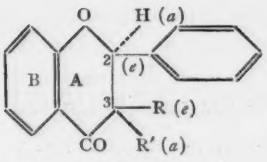
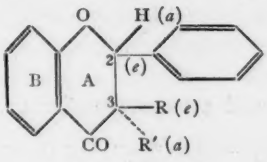


FIG. 4. Side view.: side phenyl omitted.

FIG. 4. Hydrogen atom in the 2-position and hydroxyl in the 3-position are axial and trans while hydrogen in the 3-position is equatorial.



(VI)



(VII)

a R=R′=H
b R=OH; R′=H
c R=H; R′=OH

(*d*) axial
(*e*) equatorial
— β orientation
--- α orientation

In the case of 3-hydroxy flavanones more forms can arise depending on the dispositions of the hydroxyl in the 3-position. In a stable naturally occurring from it would be reasonable to expect that the bulkier hydroxyl group would occupy the equatorial position (C-OH equatorial) leaving the C-H bond axial being α or β. Since each of these restricts automatically the disposition of the C-H axial bond in the 2-position, there can be only two stereoisomeric naturally occurring flavanolones. In them the two C-H bonds in the 2 and 3-positions being axial and trans (VI *b* and VII *b*), the requirements for ready elimination of hydrogen atoms are satisfied[27] and they readily yield the corresponding flavonols under mild conditions as already explained.

Among the synthetic methods the first method may be expected to yield racemates having the same configuration as the natural compounds because in the original flavonol structure (planar) the phenyl and the hydroxyl groups are necessarily linked by equatorial bonds and since they are bulky groups the introduction of hydrogen by reduction will not alter their equatorial arrangement. This is supported by the behaviour of dihydroquercetin (I *b*) (obtained by the reduction of quercetin) which undergoes ready dehydrogenation by boiling with dilute sulphuric acid. The second method involves ring closure. Here too the bulkier groups, *i.e.*, phenyl and hydroxyl would naturally be expected to take up the equatorial positions and the properties of the compounds are in agreement. The conditions seem to be different in the case of the third method of synthesis involving substitution by means of iodine and silver acetate[11] and by Fenton's reagent.[15]. The behaviour of the products, that is ready dehydration would suggest that the hydroxyl group in the 3-position is now linked by an axial bond (VI *c* and VII *c*) and this along with the C_2-H (axial) suffers trans elimination as water. Even the behaviour of these samples with iodine and sodium or potassium acetate would suggest this orientation of the hydroxyl group. It then follows that in substitution reactions of simple flavanones the axial hydrogen in the 3-position (VI *a* and VII *a*) is more reactive and this should be attributed to steric factors.

In the flavanone structure the axially linked atoms are less sterically hindered as compared to the equatorial ones. In this respect these structures differ from cyclohexane derivatives in which the axially linked positions are sterically hindered[28] and are not readily available for substitution reactions.

Examining the details of the behaviour of these 3-hydroxy flavanones obtained by substitution (method 3) it appears that they consist predominently of the type (VI *c*) and (VII *c*) with C-OH axial. In their reactions with sulphuric acid, besides flavones only very small amounts of the corresponding flavonols seem to be formed. This may mean that the synthetic product was a mixture having as a very minor component the more stable variety with the C-OH equatorial or it may be that the sample consisted only of one entity (C-OH axial) and a small transformation into the more stable (C-OH) equatorial variety took place during the course of treatment with sulphuric acid. A similar explanation could be given for the behaviour of these compounds with regard to iodine and sodium acetate in alcohol or acetic acid solutions. This reaction is very slow obviously due to the difficulty of an elimination reaction in which an equatorial hydrogen is involved and hence considerable quantity of the unchanged compound is recovered from the alcoholic solution. The iodo compound which is the major product may have involved substitution of the less accessible equatorial C-H in the 3-position, and its subsequent elimination is not easy and requires treatment with pyridine. There is another possibility which should not be overlooked. Because of the peculiar conditions of the hydroxy flavanone structure with C-OH bond axial, the C_2-H (axial) group (VI *c* and VII *c*) may undergo substitution comparatively more easily. Even here the subsequent elimination will be difficult and would require pyridine for its removal along with the equatorial hydrogen of the carbon atom 3.

Deviations have, however, been observed when using Zemplen's method[10] or lead tetra-acetate[14] for the synthesis of 3-hydroxy flavanones (I) by substitution. As already mentioned these methods are found to yield a mixture of 3-hydroxy flavanone and flavone. The simplest and the most satisfactory explanation appears to be that as an initial step a 3-acetoxy (axial) compound is produced by the ready substitution of C_3-H (axial) of the flavanone. Because of the higher temperature and the solvents employed, (trans) elimination of acetic acid takes place readily to yield flavone and at the same time there is partial configurational change to produce C_3-acetoxy (equatorial) flavanone. When subjected to treatment with dilute sulphuric acid and air the resulting 3-hydroxy flavanones undergo dehydrogenation to yield flavonols as observed.

In view of the abovementioned possibility of change in configuration by treatment with reagents, a sample of 3-hydroxy naringenin (IV *c*) obtained by the synthetic method (3) was treated with alcoholic sodium acetate which is known to be good for bringing about enolisation[29] as a preliminary to configurational change. The product was found to behave similar to the natural compounds and underwent ready dehydrogenation with sulphuric acid. Hence the possibility of the configurational change from the less stable C_3-OH (axial) to the more stable C_3-OH (equatorial) form is confirmed. This seems to take place even in the presence of potassium carbonate in acetone solution and may account for the partial dehydrogenation to flavonol brought about by this reagent even with 3-hydroxy flavanones prepared by Fenton's oxidation[15] or iodine and silver acetate method.[11]

Experimental

Oxidation of pinobanksin (*IV* a) *with alkaline hydrogen peroxide*

Pinobanksin (200 mg.) was dissolved in methanolic potash (20 c.c.; 4%), hydrogen peroxide (2 c.c.; 100 vol.) added and the mixture allowed to stand at room temperature for 24 hours. On dilution with water to 200 c.c. and acidification, a yellow solid separated and it crystallized from aqueous alcohol as yellow prismatic rods, m.p. 214–15°. It gave a reddish brown colour with ferric chloride, an orange colour with magnesium and hydrochloric acid and a pale yellow colour with zinc and hydrochloric acid. Its m.p. agreed with that of galangin (V *a*) and the mixed m.p. was undepressed. Yield 100 mg.

Dehydrogenation using bismuth acetate

(*a*) *Taxifolin* (*I* b).—Taxifolin (300 mg.) was added to a mixture of basic bismuth carbonate (500 mg.), acetic acid (5 c.c.) and amyl alcohol (50 c.c.) and refluxed at 140° for 1½ hours. The solvents were removed under reduced pressure and the residue extracted with aqueous borax solution. On acidifying the solution a deep yellow solid separated which crystallised as yellow needles from aqueous alcohol m.p. 306–08°. It gave a greenish brown colour with alcoholic ferric chloride, red colour with magnesium and hydrochloric acid and a mixed m.p. with quercetin (II *b*) was undepressed. Yield 200 m.g.

(*b*) 3-*Hydroxy naringenin* (*IV* c) *obtained by method* (3)[15].—3-Hydroxy naringenin (50 mg.) was oxidised by bismuth acetate as in the above case and it yielded kæmpferol (V *c*) (25 mg.).

Dehydration with acetic anhydride

(*a*) *Pinobanksin* (*IV a*).—Pinobanksin (100 mg.) was refluxed with acetic anhydride (1 c.c.) for 2 hours and the reaction mixture poured on crushed ice (50 g.). The resinous solid was first purified by the use of ethyl acetate, light petroleum mixture. It then crystallised from aqueous alcohol as colourless needles, m.p. 190° agreeing with chrysin diacetate. Yield 25 mg.

(*b*) *Synthetic* 3:5:7-*trihydroxy flavanone* (*IV* a) *prepared by method* (3)[15] —The compound (100 mg.) was subjected to dehydration with acetic anhydride as in the case of pinobanksin and it yielded chrysin diacetate (60 mg.).

Action of 2*N sulphuric acid*

(*a*) *On dihydroquercetin* (*I* b), *prepared by method* (1)[3]: 2N sulphuric acid (50 c.c.) was added to dihydroquercetin (200 mg.) and heated on a water-bath. The solution turned yellow after 3 hours and a yellow substance started separating after about 12 hours. After 30 hours the mixture was extracted with ether, the ether removed and the residue crystallised from aqueous alcohol, m.p. 308–10°. It gave a greenish brown colour with alcoholic ferric chloride, red colour with magnesium and hydrochloric acid and the mixed m.p. with quercetin was undepressed. Yield 120 mg.

(*b*) *On dihydrorhamnocitrin* (*IV* e), *prepared by method* (2)[7].—Dihydrorhamnocitrin (100 mg.) was heated with 2 N sulphuric acid for 30 hours. A yellow solid separated which crystallised as yellow needles from alcohol, m.p. 220–22°. It gave a green colour with ferric chloride, a red colour with magnesium and hydrochloric acid and a green fluorescence with concentrated sulphuric acid. Its m.p. and colour reactions thus agreed with those of rhamnocitrin (V *e*). Yield 60 mg. With acetic anhydride and pyridine it yielded 3:5:4′-triacetoxy-7-methoxy flavone, m.p. 200–01°.

(*c*) *On* 3-*hydroxy naringenin* (*IV* c), *made by Fenton's oxidation*.[15]— 3-Hydroxy naringenin (50 mg.) was heated with 2 N sulphuric acid as in the above case. A pale yellow solid separated which crystallised as pale yellow needles from alcohol, m.p. 338–42°. It gave a violet colour with alcoholic ferric chloride, a red colour with magnesium and hydrochloric acid and agreed in m.p. and mixed m.p. with apigenin.

The alcoholic mother liquor was subjected to circular paper chromatography using phenol-water mixture (upper layer) as the irrigating solvent. A yellow ring was observed having R*f* value of 0·24. On spraying with ammonia the original yellow ring turned orange-red and a fresh yellow ring with R*f* value of 0·44 was observed. An authentic sample of kæmpferol under the same condition gave an R*f* value of 0·24 while apigenin gave an

Rf value of 0·44. Thus the mother liquor was found to contain a mixture of apigenin (major component) and kæmpferol (minor component).

Iodine oxidation: (i) *alcohol and sodium acetate*

(*a*) *Natural* 3-*hydroxy flavanones.*—To a boiling solution of the compound (200 mg.) in rectified spirit (5 c.c.) was added dropwise a solution of iodine (160 mg.) and sodium acetate (1 g.) in rectified spirit (10 c.c.) during half an hour. Refluxing was continued for another 30 minutes, the alcohol distilled off and the residue treated with sulphur dioxide water. The pale yellow solid was first purified by the precipitation of coloured impurities from an ethyl acetate solution using light petroleum and finally crystallised from aqueous alcohol. The compounds thus obtained were characterised by positive magnesium and hydrochloric acid colour, m.p. and mixed m.p. with authentic samples. They also yielded orange to orange-red coloured lead salts. The results are given below:

	Oxidation product	Approximate Yield
Pinobanksin (IV *a*)	Galangin (V *a*)	45%
Pinobanksin-7-methyl ether (IV *j*) ..	Izalpinin (V *j*)	40%
Taxifolin (I *b*)	Quercetin (II *b*)	60%
Aromadendrin (IV *c*)	Kæmpferol (V *c*)	60%

(*b*) *Dihydro-quercetin* (*I* b) *prepared by method* (1).—Dihydroquercetin for this purpose was prepared by Geissman and Lichner's[3] modification of Pew's method. On oxidation with iodine and sodium acetate as in the above experiments it yielded quercetin (II *b*) in about 60% yields.

(*c*) 3-*Hydroxy naringenin* (*IV* c), *prepared by iodine and silver acetate method*[11].—The compound (200 mg.) was subjected to iodine oxidation according to the above procedure. The crude orange coloured solid product was first purified by the use of ethyl acetate, light petroleum mixture and then dissolved in methanol (0·5 c.c.) and allowed to stand in the refrigerator for 2 days. A solid separated which crystallised from aqueous alcohol as yellow needles, m.p. 276–78°. It gave a red colour with magnesium and hydrochloric acid and agreed in m.p. and mixed m.p. with an authentic sample of kæmpferol (V *c*). Yield 20 mg.

The alcoholic mother liquor was evaporated and the residue dried. It was then dissolved in 20 c.c. of boiling ethyl acetate and allowed to cool. After standing for about 24 hours in a refrigerator a small amount of pale yellow crystals appeared which turned black on filtration. Even after a recrystallisation the crystals turned brownish-black as soon as the solvent

dried up. The black solid responded to qualitative tests for iodine and decomposed even below 60°. Yield 40 mg. On concentration of the ethyl acetate mother liquor a solid was obtained which crystallised from aqueous alcohol as stout prisms, m.p. 238–40° agreeing with the original sample of 3-hydroxy naringenin. Yield 60 mg. This recovered 3-hydroxy naringenin was again subjected to iodine oxidation when it yielded 20 mg. of the iodo compound but no kæmpferol.

The iodo compound mentioned above (50 mg.) was dissolved in dry pyridine (0·5 c.c.) and heated on a boiling water-bath for 2 hours. Dilute hydrochloric acid (15%; 10 c.c.) was added and the solution extracted with ether. After evaporating the ether solution the residue was crystallised from aqueous alcohol yielding yellow needles melting at 276–78°. Its colour reactions, m.p. and mixed m.p. showed identity with kæmpferol (V *c*). Yield 20 mg. 3-Hydroxy naringenin obtained by Fenton's oxidation also behaved in a similar way.

(*d*) 3-*Hydroxy hesperetin* (*I* f), *prepared by iodine and silver acetate method*[11].—The compound (200 mg.) was subjected to iodine oxidation and the product worked up as in the above experiment. A small amount of a substance (15 mg.) separated from alcohol, m.p. 259–60°. It gave a red colour with magnesium and hydrochloric acid, an olive brown colour with alcoholic ferric chloride and agreed in m.p. with quercetin-4′-methyl ether (II *f*); mixed m.p. with an authentic sample prepared earlier by Gupta and Seshadri[30] was undepressed. An iodo compound (40 mg.) was also obtained along with the unreacted product (75 mg.). The recovered product was again subjected to iodine oxidation and just as in the previous case only an iodo compound was obtained which when heated with dry pyridine also yielded quercetin-4′-methyl ether.

(ii) *Glacial acetic acid and fused potassium acetate*

(*a*) *Taxifolin* (*I* b).—To a solution of taxifolin (500 mg.) in glacial acetic acid (10 c.c.) was added fused potassium acetate (2 g.) and iodine (420 mg.) in glacial acetic acid (5 c.c.). The mixture was refluxed for 2½ hours, acetic acid removed under reduced pressure and water added. The brownish yellow solid product was first purified by the precipitation of coloured impurities from an ethyl acetate solution using light petroleum and finally crystallised from aqueous alcohol. It agreed in its colour reactions, m.p. and mixed m.p. with quercetin. Yield 350 mg.

(*b*) 3-*Hydroxy naringenin* (*IV* c) *prepared by method* (3)[15].—3-Hydroxy naringenin (100 mg.) was subjected to iodine oxidation in acetic acid solution. The reaction products were purified and separated as in the oxidation using

alcohol and sodium acetate; kæmpferol (25 mg.) and iodo compound (35 mg.) were obtained. No unreacted product could, however, be isolated.

Attempts to prepare 3-hydroxy naringenin (IV c) by Zemplen's method.—Naringenin triacetate (1 g.) was dissolved in chloroform (20 c.c.) and bromine (0·41 g.) in chloroform (10 c.c.) was added dropwise with cooling. The mixture was exposed to ultra-violet light for 2 hours, during which hydrobromic acid was evolved. The chloroform solution was washed with water, dried over anhydrous sodium sulphate and the chloroform removed under reduced pressure. The pale yellow oil thus obtained contained bromine and could not be crystallised. It (1·1 g.) was refluxed at 140° with acetic anhydride (15 c.c.) in the presence of silver acetate (1·0 g.) for 1½ hours, filtered and poured into water. The white solid thus obtained crystallised as colourless needles from aqueous alcohol and melted over a range of 15° and could not be conveniently purified further. This acetate (600 mg.) was refluxed with alcoholic hydrochloric acid (1 : 1; 30 c.c.) for 30 minutes. On cooling an yellow solid separated (300 mg.) which crystallised from alcohol as pale yellow needles, m.p. 338–42°. It gave a yellow colour with concentrated hydrochloric acid, a violet colour with alcoholic ferric chloride and a red colour with magnesium and hydrochloric acid and agreed with apigenin (V *b*), mixed m.p. undepressed.

The alcoholic mother liquor was evaporated under reduced pressure and the residue extracted repeatedly with ether. After evaporating the combined ether extract the residue was crystallised from dilute methanol when it separated as colourless rectangular prisms m.p. 239–40° (*d.*). It gave a red colour with zinc and hydrochloric acid and magnesium and hydrochloric acid and a violet colour with alcoholic ferric chloride. Yield 50 mg. It (40 mg.) was heated with 2 N sulphuric acid (30 c.c.) for 30 hours. A yellow solid separated which crystallised as yellow needles from aqueous alcohol, m.p. 276–78°. It gave a bluish green colour with ferric chloride, a red colour with magnesium and hydrochloric acid and no colour with zinc and hydrochloric acid. It thus agreed in m.p. with kæmpferol and mixed m.p. was undepressed. Yield 25 mg.

Isomerisation of 3-hydroxy naringenin (IV c) obtained by Fenton's oxidation[15].—3-Hydroxy naringenin (100 mg.) obtained by Fenton's oxidation was dissolved in alcohol (25 c.c.) and sodium acetate (15 g.) in water (10 c.c.) was added. The mixture was allowed to stand at room temperature for 24 hours, alcohol removed under reduced pressure and the remaining solution extracted repeatedly with ether. After evaporating the combined ether extract, the residue was crystallised from dilute methanol when

it separated as colourless rectangular prisms m.p. 239–40° (*d.*). It gave a pink to red colour with zinc and hydrochloric acid, a red colour with magnesium and hydrochloric acid and a violet colour with alcoholic ferric chloride. Yield 80 mg. It (70 mg.) on refluxing with 2 N sulphuric acid yielded kæmpferol (V *c*). Yield 35 mg.

SUMMARY

A number of 3-hydroxy flavanones occur in nature and several have been obtained using a number of synthetic methods. Though they behave generally in the same way when subjected to drastic methods of dehydrogenation or dehydration, those obtained by substitution of flavanones in the 3-position seem to differ markedly from others in their reactions towards mild reagents such as dilute sulphuric acid and iodine. This is attributed to stereochemical differences. In this particular synthetic method the 3-hydroxyl is axial (H_2O elimination easy) whereas in the others it is equatorial (H_2 elimination easy). In flavanones substitution of the axially disposed C-H is the favoured one because it is sterically unhindered.

ACKNOWLEDGEMENT

Our thanks are tendered to Dr. J. C. Pew for the supply of a sample of aromadendrin and to Dr. E. F. Kurth for a sample of taxifolin.

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654-55 Printed at The Bangalore Press, Bangalore City, by C. Vasudeva Rao, Superintendent, and Published by The Indian Academy of Sciences, Bangalore.

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